CHARACTERISATION OF SUGARCANE JUICE PARTICLES THAT INFLUENCE THE CLARIFICATION PROCESS

By

CCD THAI, WOS DOHERTY

Sugar Research and Innovation, Centre for Tropical Crops and Biocommodities, Queensland University of Technology, Brisbane

c1.thai@qut.edu.au

KEYWORDS: Whole Crop, Trash, Juice Particles, Clarification, Surface Chemistry.

Abstract

Problems associated with processing whole sugarcane crop can be minimised by removing impurities during the clarification stage. As a first step, it is important to understand the colloidal chemistry of juice particles on a molecular level to assist development strategies for effective clarification performance. This paper presents the composition and surface characteristics of colloidal particles originating from various juice types by using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), X-ray photoelectron spectroscopy (XPS) and zeta potential measurements. The composition and surface characteristics of colloidal juice particles are reported. The results indicate that there are three types of colloidal particles present viz., an aluminosilicate compound, silica and iron oxide, with the latter two being abundant. Proteins, polysaccharides and organic acids were identified on the surface of particles in juice. The overall particle charge varies from –2 mV to –6 mV. In comparison to juice expressed from burnt cane, the zeta potential values were more negative with juice particles originating from whole crop. This in part explains why these juices are difficult to clarify.

Introduction

Whole crop harvesting leads to an increase in biomass compared to green and burnt cane harvesting. Excess biomass obtained from the process could potentially provide additional revenue streams to the sugar industry to overcome fluctuating raw sugar prices. However, processing juice expressed from green cane stalk and trash (i.e. tops and leaves, the non stalk component) has lead to poor clarification performance and reduced sugar quality (Moller *et al.*, 2010).

Studies on the composition of juice expressed from green cane stalk and trash have been reported previously by a number of authors (Eggleston *et al.*, 2010; Eggleston *et al.*, 2009; Muir *et al.*, 2009; Scott *et al.*, 1978). A recent study by Thai and Doherty (2011) revealed an apparent difference between the composition of sugarcane juice derived from burnt cane with all trash extracted (BE) and that from green cane with half of all trash from the entire plant extracted (GE). The role of additional impurities derived from trash is not known. Not only does the composition of juice derived from green cane stalk and trash influence clarification performance, but the additional input of fibrous material leads to

problems with sugar milling efficiencies and the quality and yield of the final raw sugar product (Kent, 2007; Kent *et al.*, 2010; McGuire *et al.*, 2011; Moller *et al.*, 2010).

Despite considerable work reported in literature, there has not been a detailed study on the coagulation and flocculation behaviour of colloidal juice particles originating from GE and from green cane harvesting with all trash unextracted (GU). Colloidal particles are classified as a suspension of particles smaller than 10 µm (Shaw, 1992). The interaction and interface of colloidal particles play a very important role in determining the physicochemical characteristics of clarified juice (CJ) (Shaw, 1992). The main forces exerted on juice particles involve gravity, van der Waals attraction and Brownian motion (Doherty and Rackemann, 2009). Particle collisions which involve particle-particle, particle-precipitate and precipitate-precipitate interactions are responsible for the type of floc structure formed. Hence, the structure of flocs impacts on clarification performance (Ching *et al.*, 1994).

The purpose of this study is to determine the nature and surface characteristics of colloidal particles present in sugarcane juice from three harvesting methods (GU, GE and BE). The identification of the type and properties of colloidal particles from different sources will provide insight into the coagulation and flocculation process, and help explain differences in the clarification behaviour of different juice types.

Materials and experimental methods

Juice sampling

Composite primary juices (PJ) obtained from GE cane were collected from the processing lines at Condong sugar mill, NSW, Australia, during the 4 week period the factory was investigating the effect of trash on factory operations. A mechanical cane harvester was used to harvest the sugarcane stalk and the speed of the harvester's fan was adjusted so that approximately half of the trash was collected. Composite PJ obtained from BE cane were also collected from the same processing lines at Condong sugar mill during the period of normal processing operations before and after the 4-week trial of processing juice expressed from GE cane. Table 1 shows the sugarcane varieties harvested during the trials.

Table 1—Details of the sugarcane varieties.

Variety	Code Name
202	Q202
203	Q203
205	Q205
210	Q210
211	Q211
5	CONCORD
26	MXD/OTHR
51	Q151
93	Q193
94	BN81-1394

Whole crop juices (GU) were obtained by harvesting whole crop in the field and expressing juice with a laboratory hammer mill. The raw juice was then diluted with deionised water to 13.5 brix and heated to 76 °C for 5 min to produce GU PJ.

All juice samples were stored at –20 °C and thawed prior to chemical analyses. All samples (GU, GE and BE) are independent juice samples and the investigation and experimentation of composite juice samples allows for juice variability and the analysis of unbiased juice samples.

Experimental Methods

Composition of colloidal juice particles

Sugarcane juice samples were centrifuged (3500 rpm, 5 min, 25°C) and the residue was further centrifuged several times after dilution with Milli-Q water in order to lower the sucrose content. The presence of sucrose causes considerable charging when the residue is exposed to an electron beam. The sample was snap frozen using liquid N_2 before freeze drying overnight. The elemental composition of polished carbon coated samples was examined using a scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM-EDX) equipped with a JEOL JXA-8200 Superprobe and operated with an acceleration voltage of 10 kV.

Surface composition of juice particles

X-ray photoelectron spectroscopy (XPS) is a useful technique which provides qualitative information on the elements and functional groups present on the interface of samples with a depth sensitivity of up to 10 nm. The XPS technique measures the energy spectra of electrons emitted when a beam of X-rays irradiates the surface of the substance placed inside a high-vacuum vessel. The diameter of analysis is approximately 10 µm and is mainly used to determine the chemical state of near surface elements.

Juice samples were filtered through a polyethersulfone membrane filter under an atmosphere of N_2 gas. The membrane filters were dried in an oven vacuum at 45±2 °C overnight. Measurements were made using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer equipped with a 165 mm hemispherical electron energy analyser. The incident radiation was monochromatic Al K_α X-rays (1486.6 eV) at 150 W (15 kV, 10 mA). The relative uncertainty of the measurements is ±10%.

Effect of zeta potential on the clarification process

The effect of particle charge (zeta potential) on juice temperature and liming technique was investigated. The particle charge of juice particles was measured on the basis of the electrophoretic mobility of particles in suspension using a Malvern Zetasizer Nano ZS instrument. Particle charge measurements were conducted using a disposable capillary zeta cell. Measurements were conducted in triplicate.

The juice aliquots were diluted to 4-fold (due to concentration limits for compatibility with the zeta potential measurement) in a matrix of 15 brix sucrose solution and a concentration of 4 mM of KCl (K^+ is the major inorganic ion in a juice solution (Thai and Doherty, 2011)).

To determine the charge of the suspended juice particles without dilution, sample aliquots were diluted using different ratios (up to 10-fold) and the particle charge recorded. A linear curve (R^2=0.97) from the data points was generated and extrapolation to zero dilution gives the particle charge of juice. For subsequent analyses, juice aliquots diluted 4-fold were measured and the slope of the linear curve was used to determine the particle charge of juice without dilution. The results obtained using this approach was similar to those of (Crees, 1988).

Sugarcane juice samples (52 °C and 76 °C) were adjusted to pH 4 (initial pH of PJ samples was 5.0 ±0.5) by the addition of 10 wt% phosphoric acid and then treated with lime saccharate (CaO:sucrose:H_2O, ratio of 1:7:13) to neutralise the juice to pH 7.8. An aliquot was then obtained to measure the particle charge.

Variants of the clarification process were then investigated. The liming techniques conducted are as follows: intermediate (I, juice at 76 °C, limed to pH 7.8 then boiled); intermediate/intermediate (II, juice at 76 °C, limed to pH 6.2, heated to 76 °C again and limed to pH 7.8 then boiled); and cold/intermediate (CI, juice at 52 °C, limed to pH 6.2, heated to 76 °C again and limed to pH 7.8 then boiled). For these clarification procedures, phosphoric acid and flocculant was not added. The particle charge was measured after clarification at pH 7.8.

Particle size

For particle size measurements, a Malvern Mastersizer 1000 was used to obtain light scattering data to determine the particle size of the juice samples. The average size of particles from each sample was obtained from five replicate measurements.

Results and discussion

Size and composition of juice particles

Samples of GU, GE and BE juices were analysed via small angle light scattering to obtain particle size data. The average particle sizes of all the PJs were all 40±5 μm. Figure 1 shows the particle size distribution of the juice samples analysed.

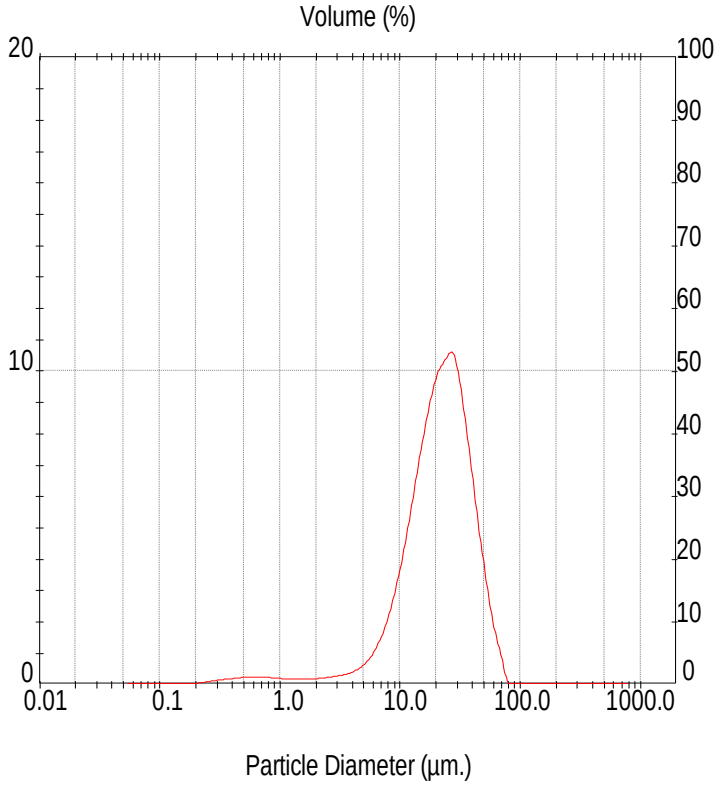

Fig. 1—Typical particle size distribution of a juice sample.

The composition of these colloidal particles were measured using SEM-EDX and the results show three types of colloidal particles are present (Figures 2, 3 and 4). Figures 2 and 3 shows the major components of colloidal juice particles are an aluminosilicate compound (originating from clays present in soil) and silica (from soil and cane plant) respectively. The third component, which is a minor component, is iron oxide (Figure 4), which is likely rust from harvesting equipment and factory processing units.

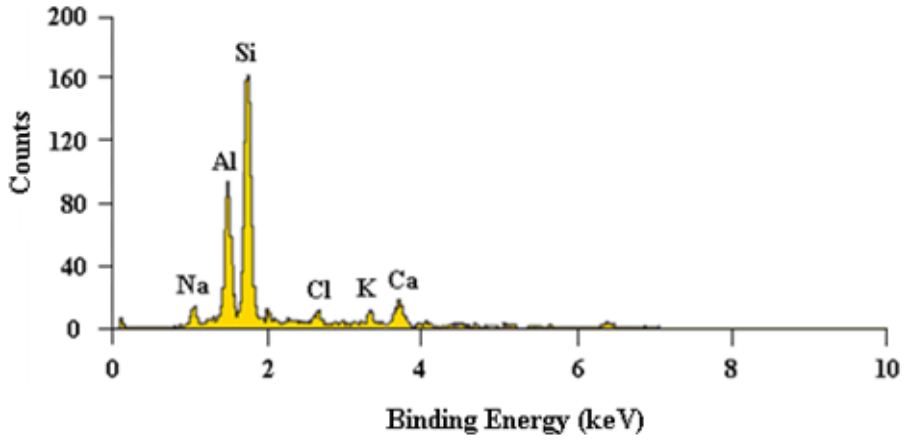

Fig. 2—Energy dispersive spectrum of a typical juice sample showing the presence of an aluminosilicate compound.

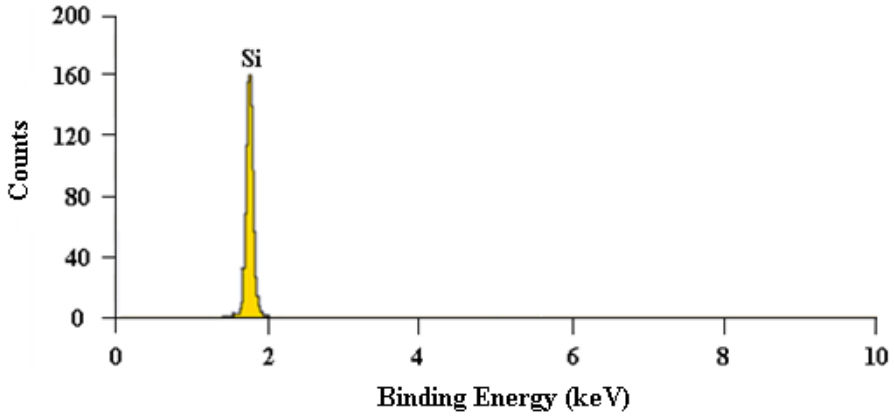

Fig. 3—Energy dispersive spectrum of a typical juice sample showing the presence of silica.

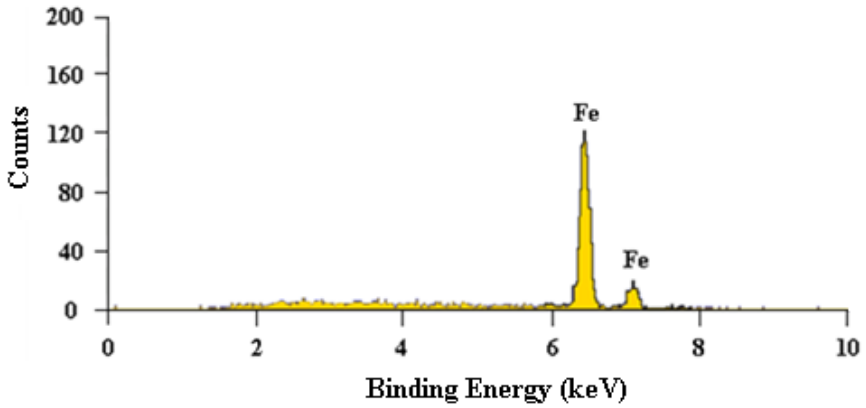

Fig. 4—Energy dispersive spectrum of a typical juice sample showing the presence of iron oxide.

Surface composition of juice particles

The XPS survey scan (Figure 5) obtained for the analysis of the surface of colloidal juice particles shows that there is a significant amount of C and O atoms and small amounts of N atoms. The signal observed at 400 eV indicates that N is present in the form of an amine or a polypeptide fragment of a protein. Table 2 shows the atomic mass percentage of these atoms to give a comparison of the relative amounts of each atom present in GU, GE and BE juice samples analysed. The results show the N content of GU is almost triple and GE is almost double than that of the BE sample. The interface of GU colloidal particles were comprised of mostly C atoms in comparison to the interface of GE and BE. However, an opposite trend was observed for the proportion of O atoms.

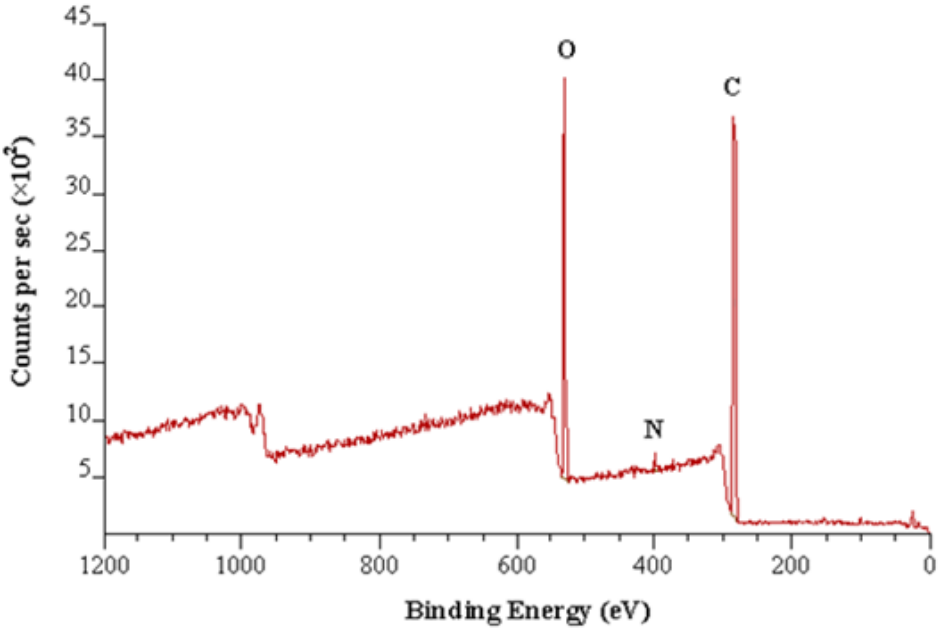

Fig. 5—XPS spectrum for a typical juice sample.

Table 2—Elemental compositions of colloidal particle interfaces.

Juice	% C*	% O*	% N*
GU	79.4	17.5	3.1
GE	70.0	27.4	2.6
BE	72.5	26.3	1.2

*Relative error, ±10%.

To investigate the functional group moieties associated with the presence C, O and N peaks, a high resolution scan was obtained. The resolved high resolution C spectrum (Figure 6) measured from the juice samples clearly indicate five chemically shifted C peaks of different bonding environments, including the more subtle shift, which is associated with the peak assigned as both the carbon adjacent to the carboxyl (C–COO) or amine group ($C–NH_2$) (Ratner and Castner, 2009).

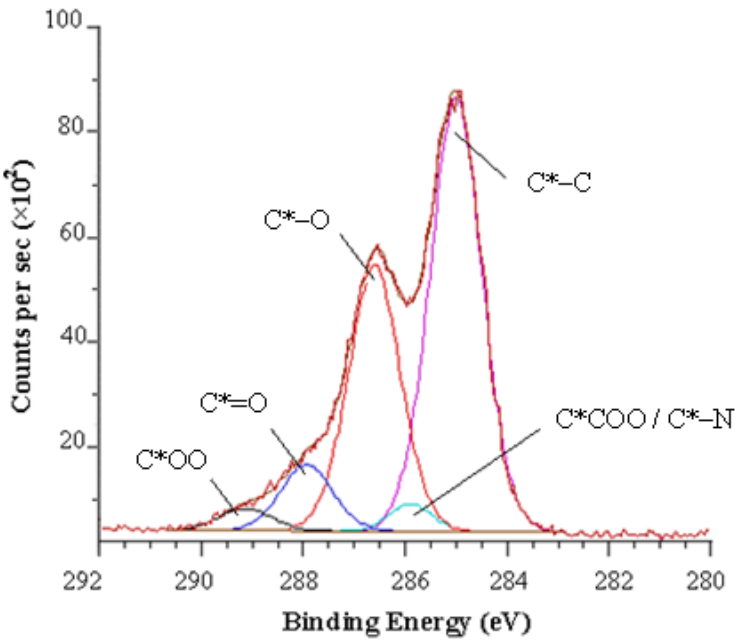

Fig. 6—The resolved high resolution C spectrum of a typical juice sample.

The XPS analysis of the samples reveal the presence of C (the asterisk refers to the C atom measured) from a hydrocarbon (C*–C), C adjacent to a carboxyl (C*–C(=O)O), C adjacent to a N atom (C*–N), C adjacent to an O atom (C*–O), carbonyl (C*=O) and ester (–C*(=O)O) group. The corresponding binding energies of these functional groups are presented in Table 3. The binding energies of each individual peak positions obtained from C, O and N in different chemical environments are consistent with those observed by other researchers (Lopez *et al.*, 1991; Ratner and Castner, 2009). Overall, these carbon functional groups are attributable to the presence of polysaccharides and organic acid compounds due to their C*–O and C*–C(=O)O linkages, respectively. The higher proportion of C–C and C–COO groups for the GU sample could be associated with the higher proportion (on the basis of atomic %) of different types of organic acids present on the particle surface.

The amine functional group (N–H_2) shown in Table 3 confirms the presence of proteins since a peak was observed at 400 eV for the respective N spectrum and also at 286 eV for the respective C spectrum. Bennett (1959) also indicated that the particle surfaces are naturally proteinaceous and are negatively charged due to the ionisation of the carboxylic acid functional groups and presence of polysaccharides, which comprise of carboxylic acid groups.

Table 3—The atomic ratios and binding energies for common functional groups on the surface of colloidal juice particles.

Functional Group/Linkage	Juice Sample					
	GU		GE		BE	
	Binding Energy (eV)	Atomic %	Binding Energy (eV)	Atomic %	Binding Energy (eV)	Atomic %
*C—C	285.0	47	285.0	35	285.0	36
O ‖ *C—C—O and *C—N	285.6	3	285.8	2	284.9	1
*C—O	286.5	21	286.6	25	286.6	29
*C═O	287.9	4	288.0	7	288.1	6
O ‖ *C—O	288.8	3	289.2	2	289.2	1
*O—H	532.9	15	532.9	25	532.9	24
*O—amide	531.6	4	531.5	3	531.4	2
*N —H_2	400.2	3	400.2	1	400.2	1

*Atom associated with the binding energy obtained from high resolution spectra.

On the basis of particle size, SEM-EDX and XPS measurements, Figure 7 shows a schematic representation of the composition of typical colloidal particles in juice. In general, on the basis of these results, the physical characteristics of colloidal juice particles derived from green cane stalk and trash differ from those of juice derived from cane with all trash extracted. Therefore, whole crop juices would influence the interactions between the surfaces of colloidal particles and ultimately affect the efficiency of the coagulation and flocculation process.

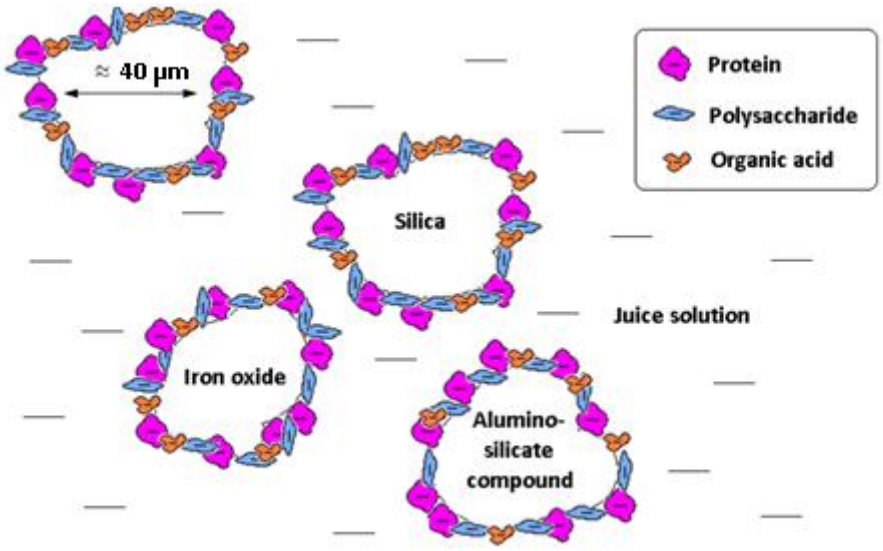

Fig. 7—A schematic representation of negatively charged materials which form the interface of typical colloidal particles in sugarcane juice.

Particle stability

Sugarcane juice is a complex system due to the high polydispersity of suspended materials (Doherty *et al.*, 2003). However, despite this, juice behaves electrophoretically as a homogeneous dispersion (Bennett, 1959). The charge of juice particles provides a good indication of the most efficient clarification method on the basis of particle stability and the removal efficiency of impurities. The closer the charge is to zero, the more likely the particles will become unstable, coagulate and separate from the liquid phase. Table 4 shows that the charges of GU, GE and BE particles are between –2 mV and –6 mV. The particle charge values also agree with the work conducted by Doherty *et al.* (2003) who reported values between –2 mV and –5 mV for sugarcane juice obtained in the Mackay region.

Table 4. Particle charge (mV) at pH 7.8 of GU, GE and BE Juices from the Condong Region.

Liming Technique	Juice Sample		
	GU*	GE*	BE*
I Liming	-4.76	-3.32	-2.48
II Liming	-4.64	-3.28	-2.64
CI Liming	-4.72	-3.44	-2.84
52 °C	-4.60	-3.80	-3.20
76 °C	-5.60	-4.48	-3.68

*Error in analysis, ±5%.

As shown in the previous section, the surface of colloids in juice consists primarily of negatively charged materials such as proteins, polysaccharides and organic acids. As these compounds are polar and the fact that lime saccharate has a solubilising effect on proteins, these compounds adsorb onto the surface and therefore form the major interface between the juice particles and the bulk phase (Bennett, 1957). Thus, proteins and polysaccharides will contribute to the coagulation and flocculation process. The higher proportion of these compounds on the surface of GU and GE particles will affect the clarification behaviour more than with BE juices.

The best clarification method for BE juices was I liming (Table 4). The charges of GU and GE colloidal particles obtained from variants of the liming techniques were less negative for the II liming technique; hence lower juice turbidities are expected since coagulation is effective when the charge is close to zero. The GU particles resulted with a more negative charge for each liming technique compared to the particle charges of GE and BE juices.

The juice samples were also limed at 52 °C and 76 °C to see the effect of temperature on particle charge. Clarification at 52 °C indicated that the particles are likely to coagulate more effectively than at 76 °C. However, more calcium phosphate will be formed at 76 °C than at 52 °C due to the solubility effect. This will lead to more effective removal of suspended solids and impurities because of the larger volume of calcium phosphate flocs formed.

Conclusions

This study investigated the nature of colloidal juice particles originating from GU, GE and BE PJ samples. Colloidal juice particles were observed to consist of an aluminosilicate compound and silica, with a minor amount of iron oxide. The surface of colloidal particles consisted of proteins, polysaccharides and organic acids. The surface of GU samples measured had a higher proportion of protein in comparison to the surface of GE and BE samples. The GU juice particles have a more negative charge than GE and BE samples, suggesting they will be more difficult to destabilise/clarify.

Future work into the effect of various coagulants and flocculating agents on the clarification performance on GU, GE and BE juices is currently being planned.

Acknowledgements

The project was funded by Sugar Research and Development Corporation, Sugar Research Limited and Queensland University of Technology. The authors thank the staff at Condong Mill for providing the juice samples. The authors also thank both Dr. Shane Askew (Advanced Analytical Centre, James Cook University) and Dr. Barry Wood (Centre of Microscopy and Microanalysis, University of Queensland) for their assistance with the SEM-EDX and XPS analyses, respectively.

References

Bennett MC (1957) Behaviour of adsorbed protein in cane sugar juice. *Journal of Colloid Science* **12**, 434-451.

Bennett MC (1959) The factors affecting stability and flocculation in cane juice. *International Sugar Journal* **61**, 77-80.

Ching HW, Tanaka TS, Elimelech M (1994) Dynamics of coagulation of kaolin particles with ferric chloride. *Water Research* **28**, 559-569.

Crees OL (1988) *The flocculation of cane sugar muds in Australian raw sugar factories.* Thesis (PhD) James Cook University of North Queensland, Townsville.

Doherty WOS, Fellows CM, Gorjian S, Senogles E, Cheung WH (2003) Flocculation and sedimentation of cane sugar juice particles with cationic homo- and copolymers. *Journal of Applied Polymer Science* **90**, 316-325.

Doherty WOS, Rackemann DW (2009) Some aspects of calcium phosphate chemistry in sugarcane clarification. *International Sugar Journal* **111**, 448-454.

Eggleston G, Grisham M, Antoine A (2010) Clarification properties of trash and stalk tissues from sugar cane. *Journal of Agricultural and Food Chemistry* **58**, 366-373.

Eggleston G, Grisham M, Tew T, Triche R, Antoine A (2009) Potential biomass quantity and sugar processing quality of trash and stalk tissues by different US sugarcane varieties. *International Sugar Journal* **111**, 108-118.

Kent GA (2007) The effect of trash on the operation and performance of a raw sugar factory. *Proceedings of the International Society of Sugarcane Technologists* **26**, 1622-1628.

Kent GA, Moller DJ, Scroope PD, Broadfoot R (2010) The effect of whole crop processing on sugar recovery and sugar quality. *Proceedings of the Australian Society of Sugar Cane Technologists* **32**, 559-572.

Lopez GP, Castner DG, Ratner BD (1991) XPS O 1s binding energies for polymers containing hydroxyl, ether, ketone and ester groups. *Surface and Interface Analysis* **17**, 267-272.

McGuire PJ, Inderbitzin M, Rich B, Kent GA (2011) The effect on whole crop harvesting on crop yield. *Proceedings of the Australian Society of Sugar Cane Technologists* **33**, 1-12.

Moller DJ, Broadfoot R, Bell S, Bakir H (2010) Whole crop processing at Broadwater mill: impacts on process operations. *Proceedings of the Australian Society of Sugar Cane Technologists* **32**, 573-587.

Muir BM, Eggleston G, Barker B (2009) The effect of green cane on downstream factory processing. *Proceedings of the South African Sugar Technologists' Association* **82**, 164-199.

Ratner BD, Castner DG (2009) 'Electron Spectroscopy for Chemical Analysis'. 2nd edn (John Wiley and Sons:Chichester).

Scott RP, Falconer D, Lionnet GRE (1978) A laboratory investigation of the effects of tops and trash on extraction, juice quality and clarification. *Proceedings of the South African Sugar Technologists' Association* **52**, 51-53.

Shaw DJ (1992) 'Introduction to Colloid and Surface Chemistry'. 4th edn (Butterworth Heinemann:Oxford).

Thai CCD, Doherty WOS (2011) The composition of sugarcane juices derived from burnt cane and whole green cane crop *Proceedings of the Australian Society of Sugar Cane Technologists* **33**, 1-9.